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Docket No. 0756-1894

In re Patent Application of
Shunpei YAMAZAKI et al.
Serial No.: 09/197,534
Filed: November 23, 1998
For: LASER PROCESS
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VERIFICATION OF TRANSLATION

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir:

I, Satomi Yumoto, B-310, 304-1, Hase, Atsugi-shi, Kanagawa-ken 243-0036 Japan, a translator, herewith declare:
that I am well acquainted with both the Japanese and English Languages;
that I am the translator of the attached translation of Japan Patent Application No. 4-252295 filed on August 27, 1992; and
that to the best of my knowledge and belief the following is a true and correct translation of Japan Patent Application No. 4-252295 filed on August 27, 1992.
I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: this 20 day of March, 2002

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 [Attachment] Figure 1
 [Attachment] Abstract 1

[Name of Document] Specification

[Title of Invention] LASER PROCESS METHOD

[Scope of Claims]

[Claim 1]

In a laser process method comprising the step of irradiating laser pulses with a wavelength of 400 nm or shorter and a pulse width of 50 nsec or less to a film mainly including the Group IV element and having been irradiated with a high energy impurity ion so as to activate a semiconductor, said method characterized in that a film with a thickness of 10 to 100 nm mainly including oxide silicon is formed on the said film, and a relation $\log_{10} N \leq -0.02 (E - 350)$ is satisfied between an energy density $E [mJ/cm^2]$ of irradiation of the laser and the number N of the laser pulses.

[Claim 2]

A laser process method according to claim 1, wherein the laser light for use is a KrF excimer laser, an ArF excimer laser, a XeCl excimer laser or XeF excimer laser.

[Claim 3]

A laser process method according to claim 1, wherein phosphorus, boron or both thereof is used as the impurity ion.

[Detailed Description of the Invention]

[0001]

[Technical field to which the invention belongs]

The present invention relates to a highly reliable laser annealing process method suited for use in mass production of semiconductor devices, which enables uniform annealing at high yield. Particularly, the present invention provides a laser annealing process of a film whose crystallinity had been greatly impaired by the damage of processes such as ion irradiation, ion implantation and ion doping.

[0002]

[Prior Art]

Recently, methods of lowering of process temperatures of semiconductor devices are extensively studied. As one of the reasons, it is because fabricating semiconductor devices on an insulating substrate of glass etc. is needed. The laser annealing technology is being watched as the ultimate low temperature process.

[0003]

[Problems to be solved by the Invention]

However, conventionally, the conditions for laser annealing have not been discussed enough because each apparatus or each film has its own conditions. As a result, it has been considered that the laser annealing technology varies too widely to make practicable. The object of the present invention is to indicate the conditions that have never been recognized to obtain a highly reproducible result by a laser annealing process.

[0004]

[Means for solving the Problems]

The present inventor has searched for the optimum conditions of a laser annealing process with an aim to activate films, wherein a film is considerably damaged by processing such as ion irradiation, ion implantation and ion doping, and is thereby impaired in crystallinity as to yield an amorphous phase or a similar state which is far from being called as a semiconductor, and then the present inventor has found that the optimum conditions fluctuates in compliance with incorporated impurities and the number of pulse shots of the laser beam as well as the energy condition of the laser beam in that case.

[0005]

In the present invention, the films to be activated mainly consist of silicon, germanium, or an alloy of silicon and germanium or the Group IV element such as silicon carbide. In laser annealing these films, it is well known that a laser beam with the wavelength of 400 nm or shorter is favorably used by taking the light transmission into consideration.

[0006]

For example, it is generally believed that the sheet resistance can be lowered if the energy density of a laser beam is sufficiently high for activation. However, in fact, in the case of containing phosphorus as an impurity, such tendency can be clearly observed, while in the case of containing boron as an impurity, it can be deteriorated in the high energy conversely. Moreover, it is taken for granted that the increase in pulsed shots reduces fluctuation of the effect in annealing by the pulse laser, however, it is also found that the morphology of films deteriorates with increasing number of shots to increase fluctuations in a microscopic level.

[0007]

This can be explained by the growth of crystal nuclei during forming due to a laser beam irradiation being applied to the film repeatedly. As a result, the size distribution appears within range of from 0.1 to 1 μ m inside the film which was previously composed uniformly. Particularly, this phenomenon was distinguished in the laser irradiation with high energy.

[0008]

It has been found that the film must be covered by a transparent film with a thickness of 3 to 300 nm instead of being exposed to atmosphere in laser annealing. Although such a film is preferably made of silicon oxide or silicon nitride from the viewpoint of transmitting laser beam, in general, a material mainly comprising silicon oxide is used in order to serve as a gate oxide film. Needless to say, phosphorus or boron may be doped into this with an aim to passivate the mobile ions. In the case that the film containing a Group IV element is not be covered by such a transparent film, the above-mentioned non-uniformity is more accelerated.

[0009]

Under these conditions, it has been also found that a further uniform film can be obtained by applying pulsed laser beam to satisfy the following relation additionally:

$$\log_{10} N \leq A(E - B)$$

wherein E (mJ/cm^2) is the energy density of the irradiated laser pulses and N (shots) is the number of

shots of laser pulses. The values for A and B are different depending on the impurities being incorporated in the film, A = - 0.02 and B = 350 are chosen in the case that the impurity is phosphorus and an A = - 0.02 and B = 300 are chosen in the case that the impurity is boron. The present invention will be explained in more detail referring to examples below.

[0010]

[Example]

Fig. 1 shows schematically a laser annealing apparatus used in the present example. A laser beam is generated in a generator 2, amplified in an amplifier 3 through full reflection mirrors 5 and 6, and then introduced in an optical system 4 through full reflection mirrors 7 and 8. The initial laser beam is a rectangle with about $3 \times 2 \text{ cm}^2$, but is processed into a long beam with a length of from about 10 to 30 cm and a width of from about 0.1 to 1 cm by the optical system 4. The maximum energy of the laser passing through this optical system was 1,000 mJ/shot.

[0011]

An optical path in the optical system 4 is illustrated in Fig. 5. A laser light incident on the optical system 4 passes through a cylindrical concave lens A, a cylindrical convex lens B, a fly-eye lens C of a lateral direction and a fly-eye lens D of a vertical direction. The laser light is changed from an initial gauss distribution to a rectangular distribution by virtue of these fly-eye lenses C and D. Further, the laser light passes through a cylindrical convex lenses E and F, and through a mirror G (a mirror 9 in Fig. 1), and is focused by a cylindrical lens H to irradiate the specimen.

[0012]

In this Example, distances X_1 and X_2 indicated in Fig. 5 are fixed, and a distance X_3 between a virtual focus I (which is generated by the difference between curved surfaces of the fly-eye lenses) and the mirror G, and distances X_4 and X_5 are varied to adjust a magnification M and a focal length F. That is, the following relation exists between them:

$$M = (X_3 + X_4) / X_5,$$

$$1 / F = 1 / (X_3 + X_4) + 1 / X_5.$$

In this Example, a total length X_6 of the optical path is about 1.3 m.

[0013]

The beam is modified into such a long-shaped one to improve processability thereof. That is, the rectangular beam which is irradiated onto a specimen 11 through the full reflection mirror 9 after departing the optical system 4 has a longer width as compared with that of the specimen, so that, the specimen need to be moved only along one direction as a consequence. Accordingly, the stage of the specimen and the driving apparatus 10 have simple structures and the maintenance is easy to operate. Furthermore, the alignment operation at setting the specimen can also be greatly simplified.

[0014]

On the other hand, if a beam is almost a square shape, it is impossible to cover the entire substrate only with a single beam, so that the specimen should be moved two-dimensionally like vertically or horizontally. In such circumstances, however, the driving apparatus of the stage becomes

complicated and the alignment also must be done in a two dimensional manner that it involves much difficulty. When the alignment is done manually, in particular, a considerable time is consumed for this step to greatly reduce the productivity of the entire process. Furthermore, those apparatuses must be fixed on a stable table such as a vibration proof table.

[0015]

As the specimen, various types of glass substrates (e.g., a Corning #7059 glass substrate) with 100 mm in length and from 100 to 300 mm in width were used. As the laser, a KrF laser (emitting light at a wavelength of 248 nm and at a pulse width of 30 nsec) was used.

[0016]

An amorphous silicon film was formed into 100 nm in thickness on a glass substrate by the plasma CVD (chemical vapor deposition) method. This film was annealed at 600 °C for 48 hours to crystallize, and was patterned in island-like. Furthermore, a silicon oxide film with a thickness of 70 nm was formed by the sputtering method to dope phosphorus into the entire surface of the substrate. A so-called ion doping process was employed in this step using phosphine (PH_3) as the plasma source.

The accelerating voltage of 8 kV was employed. Furthermore, a part of the substrate was masked to implant boron by ion doping process. Diborane (B_2H_6) was used as the plasma source while accelerating at a voltage of 65kV. More specifically, phosphorus was implanted into the masked portions to result in N-type, while both phosphorus and boron were implanted into the unmasked portions to result in P-type.

[0017]

Then, laser beams with various energy densities and the number of pulse shots are irradiated to activate the laser, and the sheet resistance was measured and the morphology was observed through an optical microscope. The results are shown in Figs. 2 to 4.

[0018]

Fig. 2 shows a relation of the sheet resistance of a silicon film doped with phosphorus ions, the energy density of the laser beam and the number of the pulse shots. Phosphorus was incorporated at a dose of $2 \times 10^{15} \text{ cm}^{-2}$. With a laser beam with an energy density of 200 mJ/cm² or less, a large number of shots were necessary to activate, yet with a poor result yielding a high sheet resistance of about 10 k Ω /□, while with a laser beam with an energy density of 200 mJ/cm² or higher, it was sufficiently activated with a laser irradiation of from 1 to 10 shots.

[0019]

Fig. 3 shows a laser activation of a silicon film doped with boron ions at a dose of $4 \times 10^{15} \text{ cm}^{-2}$. A larger number of shots were necessary in the case of using the energy density of 200 mJ/cm² or lower was since the energy was insufficient for the activation. In the range of from 200 to 300 mJ/cm², a sufficiently low sheet resistance was obtained with 1 to 10 shots, while with laser irradiation at an energy density of 300 mJ/cm² or higher, the sheet resistance was rather elevated. In particular, contrary to the case with a laser beam energy density of 200 mJ/cm² or lower, the sheet resistance was elevated with increasing the number of pulse shots, and this phenomenon can be explained by the

growth of grain boundary due to the impaired homogeneity of the film by applying laser irradiation for too many shots.

[0020]

In a practical process, the laser annealing is applied simultaneously to both P-type and N-type regions.

Accordingly, if a laser beam is irradiated at an energy density of 350 mJ/cm², N-type region is sufficiently activated while the properties of the P-type region is impaired. Therefore, in the process according to the present example, it is preferred that an energy density ranges from 200 to 300 mJ/cm², more preferably from 250 to 300 mJ/cm².

[0021]

As aforementioned that the morphology of the film is influenced by laser annealing, in fact, the number of pulse shots can be related to the laser beam energy density and the film morphology as illustrated in Fig. 4. In this figure, the term "Annealing Pulse" signifies the number of laser beam pulse shots. The solid circle in the figure represents the point at which a change in surface morphology is observed on a phosphorus-doped silicon, and the open circle represents the same on a boron-doped silicon. The upper region on the right hand side of the figure corresponds to a condition which yields poor morphology on the surface (rough surface), and the lower region on the left hand side of the figure corresponds to that which yields favorable morphology on the surface (smooth surface). It can be seen from the results that the phosphorus-doped silicon has a stronger resistance against laser irradiation. From this result, the condition for conducting laser annealing without impairing the surface morphology can satisfy the following relation:

$$\log_{10} N \leq A(E - B)$$

wherein E (mJ/cm²) is the energy density of the irradiated laser beam, and N (shots) is the number of shots of pulsed laser. The values for A and B are A = - 0.02 and B = 350 in the case phosphorus is incorporated as the impurity, and are A = - 0.02 and B = 300 when boron is incorporated as the impurity.

[0022]

When the morphology is considerably impaired, the characteristic values show large scattering because the properties of silicon seriously deteriorate locally. In fact, in a silicon film with a defective morphology (a rough surface), a sheet resistance was scattered more than 20 %. To reduce this scattering, the above conditions must be satisfied and the laser energy density at a pertinent value must be set.

[0023]

For instance, when a laser energy density is set at 250 mJ/cm², the laser beam is shot at a frequency of 10 times or less. When a laser energy density is set at 280 mJ/cm², the laser beam is preferably shot at a frequency of from 1 to 3 times. By conducting laser annealing under such conditions, the sheet resistance could be controlled within a fluctuation of 10 % or less.

[0024]

[Effect of the invention]

By the optimum laser annealing according to the present invention, a highly reliable semiconductor film having low fluctuation in properties was obtained. Therefore, it can be considered that the present invention is beneficial to the semiconductor industry.

[Brief Description of the Drawings]

[Fig. 1] shows a schematic view of a laser annealing apparatus used in the embodiments of the present invention.

[Fig. 2] shows the relationship between the sheet resistance of a silicon film (phosphorus-doped, N-type) obtained by laser annealing according to the embodiment of the present invention, the laser energy density and the repetition times of pulse shots.

[Fig. 3] shows the relationship between the sheet resistance of a silicon film (phosphorus- and boron-doped, N-type) obtained by laser annealing according to the embodiment of the present invention, the laser energy density and the repetition times of pulse shots.

[Fig. 4] shows the relationship between the morphology of the silicon film obtained in the embodiment of the present invention, the laser energy density and the repetition times of the pulse shots.

[Fig. 5] shows a concept of an optical system of the laser annealing apparatus used in the embodiments of the present invention.

[Description of Marks]

- 1 a stable table of an optical system
- 2 a laser apparatus (a generator)
- 3 a laser apparatus (an amplifier)
- 4 an optical system for forming beams
- 5~9 full reflection mirrors
- 10 a specimen stage and a driving apparatus
- 11 a specimen (a glass substrate)

[Name of Document] Abstract

[Abstract]

[Purpose] To offer the optimum conditions for activating a film of the Group IV element by a laser annealing.

[Construction] In activating a film, which is formed on an insulating substrate and is impaired in crystallinity by irradiation of high energy ions, by irradiating a pulsed laser beam such as an excimer laser, the energy density of laser pulses and the number of shots of laser pulses are set as follows:

$$\log_{10} N \leq -0.02 (E - 350)$$

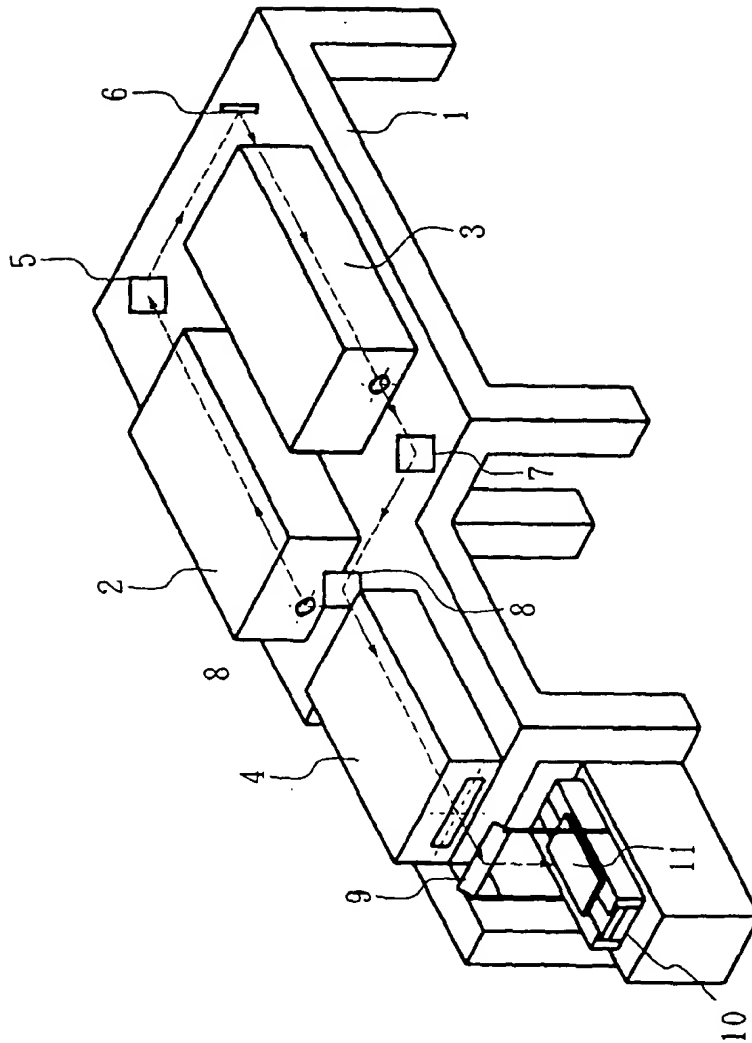
wherein E (mJ/cm^2) is the energy density of the irradiated laser pulses and N (shots) is the number of shots of laser pulses.

[Selected Figure] None

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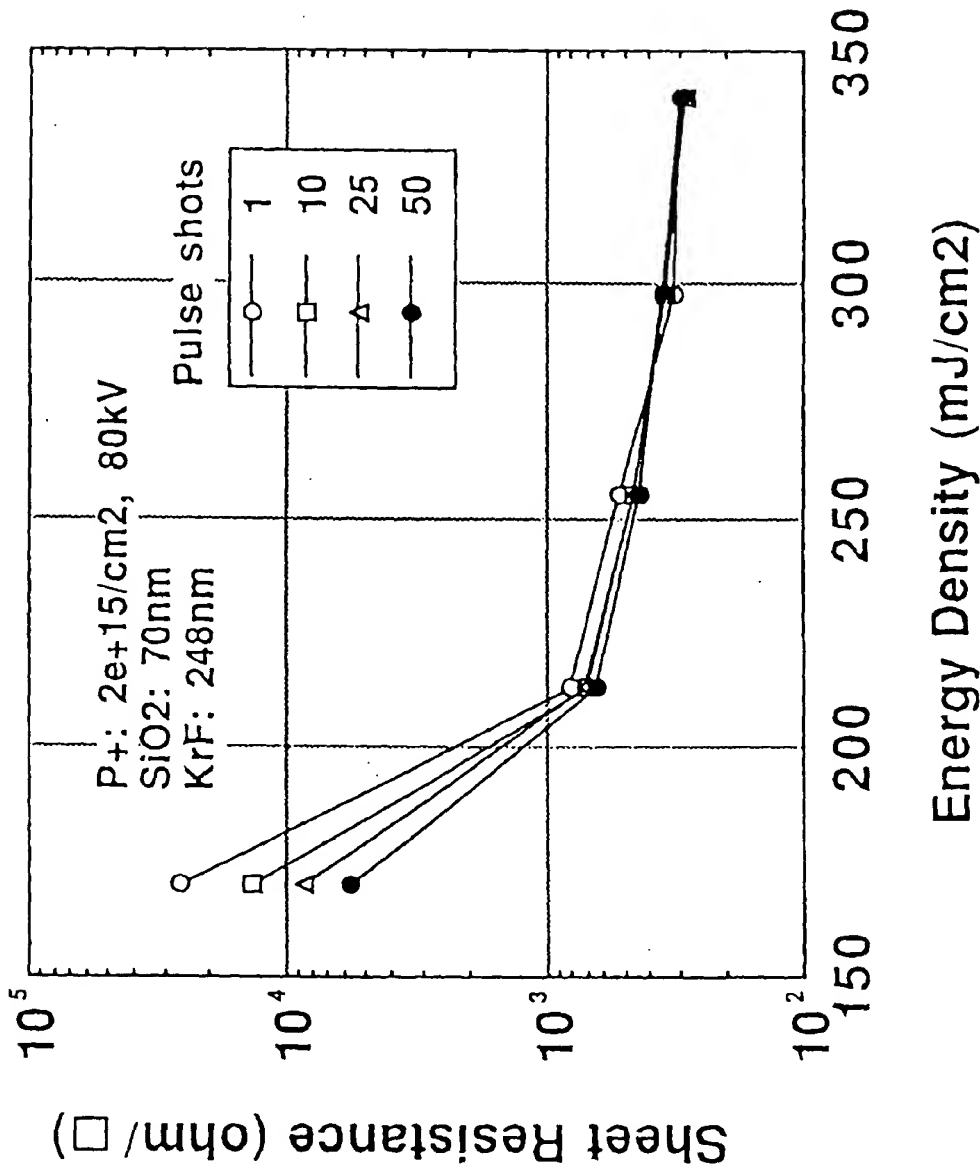
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【図 1】



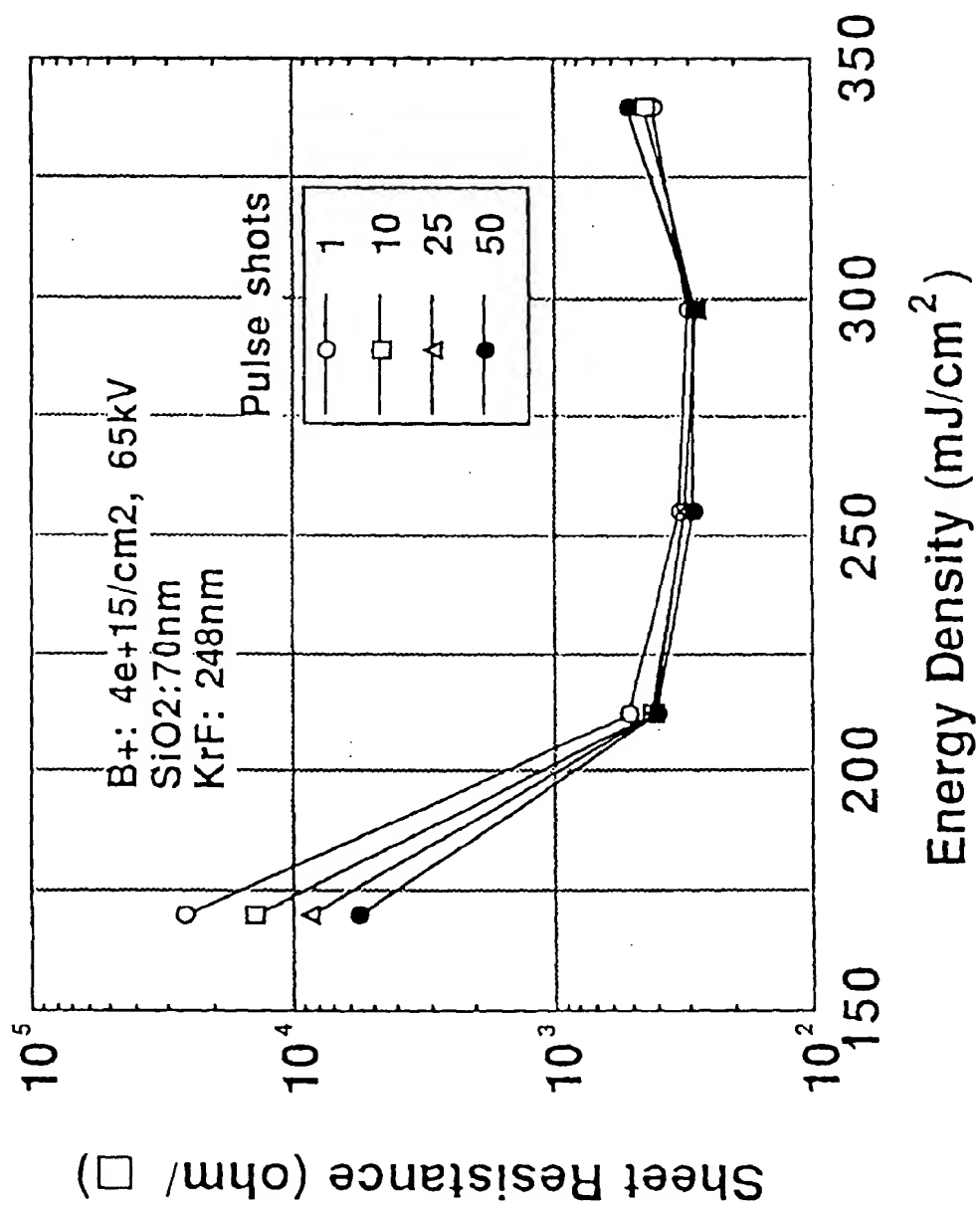
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【図 2】



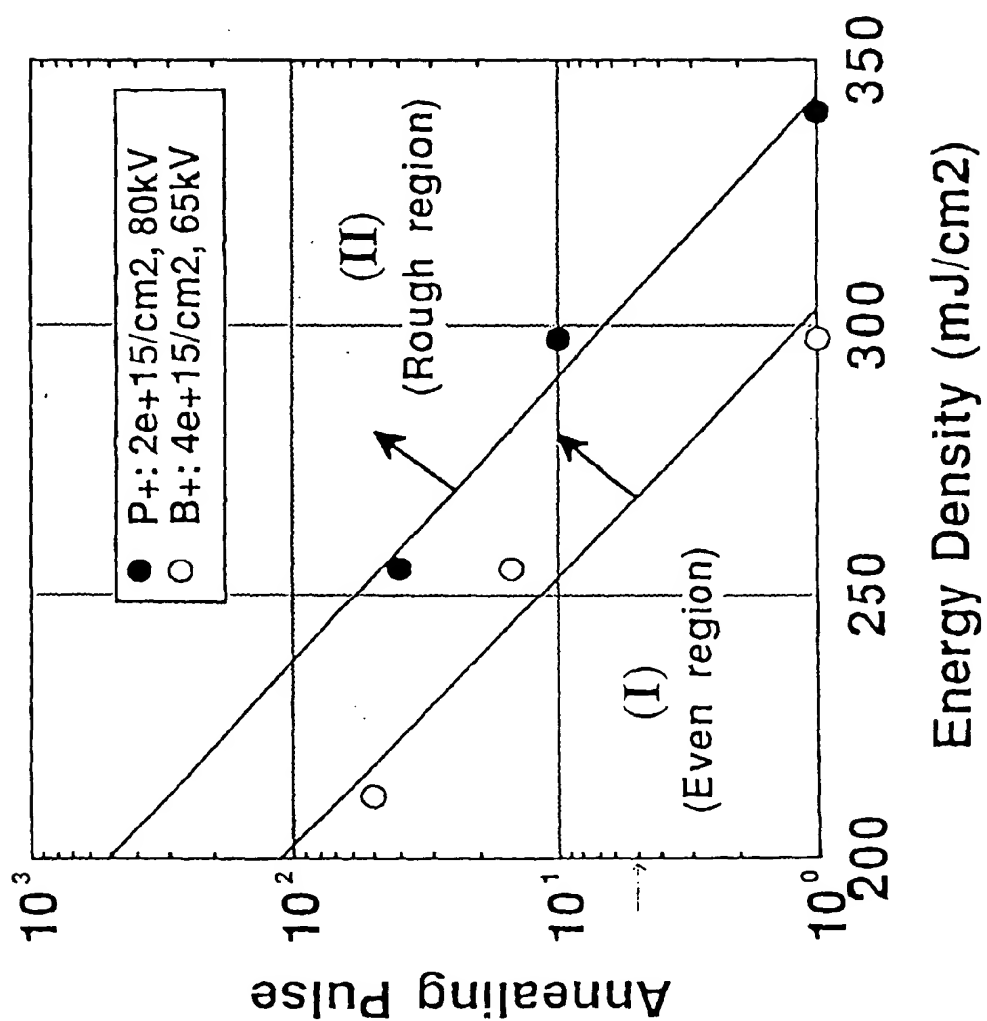
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【図 3】



【整理番号】 P002144-01

【図 4】



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【図 5】

